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AUTHOR(S): C. M. Miller and N. S. Nogar

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Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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C. M. Miller and N. S. Nogar
Group CNC-2, Mail Stop 738
Los Alamos National Laboratory, Los Alamos, NM 87545

ABSTRACT

Two color multiphoton ionization has been used to examine the spectroscopy of Lu atoms near the ionization threshold of 5.43 electron volts (43800 cm^{-1}).

INTRODUCTION

Sensitive elemental analysis of the rare earth elements, particularly with respect to isotope ratios, is often complicated by the presence of isobars which interfere with mass spectrometric analysis. Resonance or multiphoton ionization spectroscopy offers the opportunity to alleviate these interferences by selectively ionizing the species of interest, using the electronic transitions characteristic of that element. Two-photon, one-color photoionization of lutetium, using the $^2D^0_{3/2}$ intermediate level at 22125 cm^{-1}, has been shown to discriminate against isobaric ytterbium by a factor of at least 50000, while accurately reproducing the lutetium isotope ratio.[1] The use of secondary resonances, such as Rydberg or autoionization levels, offers the possibility of further selectivity, through the simultaneous matching of two resonances, and increased sensitivity, through increased cross sections for absorption near or above the ionization threshold. The intent of the current effort is to elucidate those levels in lutetium which may promote such detection techniques.

EXPERIMENTAL

A XeCl* excimer laser was used to simultaneously pump two dye laser systems for these photoionization experiments. The first, operating with pulse energies of 20 to 100 microjoules, was used to saturate the $5d6s^2\ ^2D_{3/2} \cdot 5d6s6p\ ^2D^0_{3/2}$ transition of lutetium at 22125 cm^{-1}. The second dye laser, with pulse energies up to 2 millijoules, was tuned through the spectral region corresponding to transitions from the $^2D^0_{3/2}$ state to highly excited Rydberg levels and autoionizing states. In both cases, the dye coumarin-460 was utilized, with dye laser bandwidths on the order of 0.2 cm^{-1} over the 4380 to 4780 Å tuning curve.

The dye laser beams were directed antiparallel through the ionization region of a time-of-flight mass spectrometer. Both beams were unfocussed and 3 mm in diameter. Ions thus created were extracted into the drift tube of the apparatus with a pulsed field synchronized to follow the firing of the laser. When high potentials were required for field ionization of Rydberg states, DC extraction was used. Signal processing electronics recorded the lutetium ion signal arriving at the spectrometer's electron multiplier.

Lutetium atoms for photoionization were provided by resistively heating a thin foil of the metal. Source temperatures ranged from 900 to 1200°C.

RESULTS

Figure 1 shows the observed one- (lower) and two- (upper) color, two photon photoionization spectra of lutetium. In the lower trace, a single laser was scanned over the indicated wavelength region; in the upper trace, the second laser at 22125 cm^{-1} (4519 Å) was added. Both traces are shown on the same scale and are uncorrected for the tuning curve of the laser dye. At the laser powers used, optical saturation of several transitions was observed to occur.

Table 1 lists the observed photoionization peaks, with the origin of each peak listed, and cross references to Figure 1. Four autoionization levels are observed, three of which have been previously noted.[2] In two cases, both single- and two-color transitions to the same autoionizing level are seen. Several single-color resonances are also found, corresponding to known lutetium transitions.[3]

A number of single-color resonances are found which have no origin in known lutetium transitions (peaks A-E). Some have significantly enhanced ionization probability with the addition of the 4519 Å laser ("augmented single-color"), and two (peaks D and E) have previously been assigned as autoionizing resonances.[2] The true origin of these signals is currently under investigation.

Transitions to Rydberg levels from the intermediate $^2D^0_{3/2}$ level were also observed, but were few in number due to field ionization limitations in our apparatus.

DISCUSSION

Our results indicate that the use of autoionizing levels in conjunction with resonant intermediate levels can lead to a significant increase in the ionization probability of lutetium. Power studies indicate that this increase may be as large as two orders of magnitude, compared to single-color resonance ionization under similar laser conditions.

In further efforts to increase the analytical sensitivity of the resonance ionization process, calculations have been performed using rate equations modeling.[4] These have confirmed the beneficial effect of the use of autoionizing resonances found experimentally. Results indicate that the applicable absorption cross sections are sufficient for the use of continuous wave laser excitation, with the accompanying increase in the ionization duty cycle.

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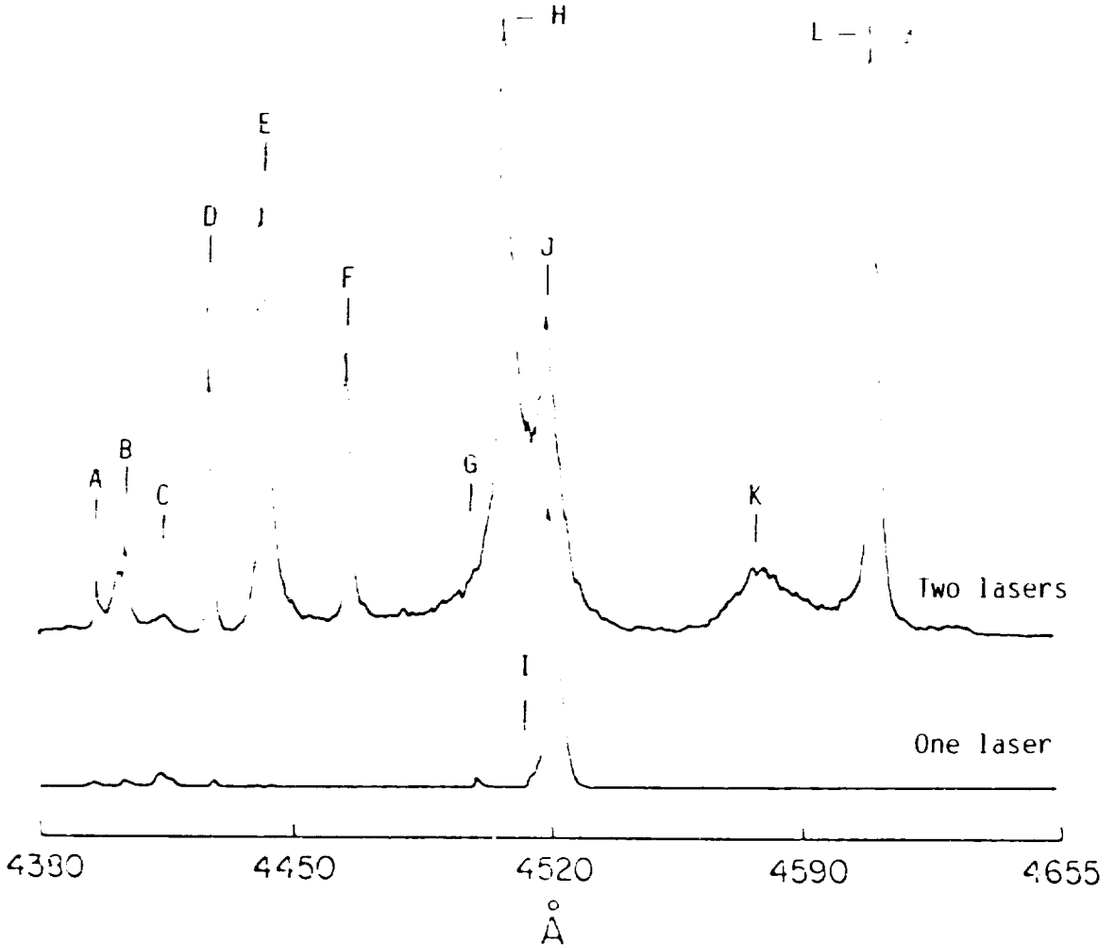

Figure 1 Photoionization Spectra of Lutetium

Table 1 Observed Photoionization Transitions

Label	Wavelength (Å)	Origin
A	4397	Augmented single-color (doublet)
B	4404	Augmented single-color (doublet)
C	4415	Single-color
D	4428	Augmented single-color
E	4443	Augmented single-color
F	4465	Two-color transition to auto-ionizing level at 44515 cm^{-1}
	4480	Single-color resonance for thermally excited lutetium
G	4499	Single-color resonance
H	4508	Two-color transition to auto-ionizing level at 44302 cm^{-1}
I	4513	Single-color transition to auto-ionizing level at 44302 cm^{-1}
J	4519	Single-color resonance (both lasers at same wavelength)
	4562	Single-color transition to auto-ionizing level at 43832 cm^{-1}
K	4576	Two-color transition to auto-ionizing level at 43973 cm^{-1}
L	4606	Two-color transition to auto-ionizing level at 43832 cm^{-1}